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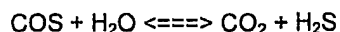
(54) Title: DESULPHURISATION

(57) Abstract: A process for the removal of carbonyl sulphide from a fluid stream comprises passing the fluid through a fixed bed of an intimate mixture of shaped units formed from particles of a carbonyl sulphide hydrolysis catalyst and shaped units formed from particles of an absorbent for hydrogen sulphide.

Desulphurisation

This invention relates to desulphurisation and in particular to the removal of sulphur compounds from fluid streams containing carbonyl sulphide.

Carbonyl sulphide can be converted to hydrogen sulphide and carbon dioxide by
5 hydrolysis with water.



This reaction is catalysed by a hydrolysis catalyst such as activated alumina. The resultant hydrogen sulphide can be removed by absorption with a suitable absorbent such as a composition containing copper, zinc, iron, manganese and/or nickel compounds such as
10 oxides, hydroxides, carbonates, or hydroxycarbonates.

Conventionally carbonyl sulphide is removed by passing the fluid (to which water has been added if necessary) through a bed of a suitable hydrolysis catalyst and then passing the effluent through a bed of a hydrogen sulphide absorbent or through an alternative hydrogen sulphide removal system. If the feedstock fluid contains hydrogen sulphide as well as carbonyl
15 sulphide, in order to shift the equilibrium towards removal of the carbonyl sulphide, the fluid may be passed through a bed of a hydrogen sulphide absorbent prior to contact with the carbonyl sulphide hydrolysis catalyst.

In some circumstances, e.g. upstream of poison-sensitive catalysts, it is desirable to achieve the minimum possible carbonyl sulphide content in the product stream.

20 We have realised that the equilibrium may be shifted further towards the conversion of the carbonyl sulphide if the hydrogen sulphide is removed as it is formed.

Accordingly the present invention provides a process for the removal of carbonyl sulphide from a fluid stream comprising passing the fluid through a fixed bed of an intimate mixture of shaped units formed from particles of a carbonyl sulphide hydrolysis catalyst and
25 shaped units formed from particles of an absorbent for hydrogen sulphide.

Both types of shaped units in the mixture may be pellets, granules or extrudates having maxima and minima dimensions in the range 0.5 to 6 mm. They each preferably have an aspect ratio, i.e. the ratio of the maximum dimension to the minimum dimension, below 2. Preferably the maximum dimension of the absorbent units is 0.5 to 2 times the maximum
30 dimension of the hydrolysis catalyst units.

The relative proportions of the absorbent and hydrolysis catalyst units will depend on the activity of the hydrolysis catalyst units under the relevant process conditions. The greater the activity, the smaller is the proportion of hydrolysis catalyst units that is required, and hence the greater the overall sulphur removal capacity of the fixed bed. The use of a mixture of
35 shaped units is advantageous compared to the use of shaped units formed from a mixture of particles of the hydrolysis catalyst and hydrogen sulphide absorbent as it is more versatile since the proportions of the units employed can be tailored to the specific application.

Preferably the hydrolysis catalyst units form 5 to 50% by volume of the mixture of units.

The hydrolysis catalyst units preferably comprise granules, pellets or extrudates of an activated alumina composition. They may contain 0% to 10% by weight of a suitable binder, for example calcium aluminate cement, to enable shaped units of adequate strength to be produced. The shaped units preferably have a BET surface area of above 50 m²/g, particularly over 100 m²/g, for example 150-400 m²/g.

The hydrogen sulphide absorbent is preferably formed from a composition containing copper and/or zinc oxides, hydroxides, carbonates or hydroxycarbonates, and preferably has a BET surface area above 50 m²/g. The absorbent may also contain other components such as alumina and may contain up to about 10% by weight of a binder such as a calcium aluminate cement. Particularly suitable hydrogen sulphide absorbents are described in US 4871710.

Although that reference indicates that shaped units, e.g. agglomerates, made from a precipitated composition containing copper, zinc and aluminium compounds and a binder can themselves be used for carbonyl sulphide removal, we have found that the use of a mixture of a carbonyl sulphide hydrolysis catalyst units and hydrogen sulphide absorbent units is advantageous, particularly at process temperatures below 80°C.

The fluid stream being treated may be passed through the bed in the liquid or gaseous state at any convenient temperature ranging from ambient, i.e. about 20°C to about 200°C and at any convenient pressure, for example ranging from atmospheric to 100 bar abs. Examples of fluid streams to which the present invention may be applied include hydrocarbon streams such as natural gas; nitrogen and/or oxygen-containing streams such as air; carbon oxides streams such as carbon dioxide; and hydrogen-containing streams such as hydrogen/carbon oxides synthesis gas mixtures.

The concentration of carbonyl sulphide in the fluid stream may vary within a wide range. Where it is more than about 100 ppm by weight, it may be desirable to decrease its concentration, prior to use as the feedstock to the process of the present invention, by an initial hydrolysis step followed by a hydrogen sulphide removal stage using for example a liquid absorbent.

Although water may be formed when the hydrogen sulphide formed by the hydrolysis is absorbed, and so is available for further hydrolysis reaction, it is preferred that the feedstock also contains some water, preferably in an amount of at least three moles per mole of carbonyl sulphide.

As an example, if a typical synthesis gas containing hydrogen and carbon oxides, with a carbon dioxide content of 3.5% by volume and containing 200 ppb by volume of carbonyl sulphide, 200 ppb by volume H₂S and 10 ppm by volume of water, is brought to equilibrium by passage through a bed of a hydrolysis catalyst at a specified temperature, the carbonyl sulphide content of the product is as shown in the following table.

Temperature (°C)	Equilibrium COS content (ppb by volume)
25	10
50	17
75	28

In a sequential system wherein a hydrogen sulphide absorbent bed is disposed downstream of the bed of hydrolysis catalyst, the carbonyl sulphide content of the product will not be lower than the equilibrium concentration.

5 In contrast, we have found that passage of such a synthesis gas through an intimate mixture of 1 volume of granules of an activated alumina hydrolysis catalyst and 4 volumes of granules of a hydrogen sulphide absorbent, comprising zinc hydroxycarbonate and 10% by weight of a calcium aluminate cement binder, at about 75°C and about 50 bar abs. pressure, with a contact time of about 15 seconds gave a product containing no detectable carbonyl sulphide or hydrogen sulphide (detection limits 2 ppb by volume). Both the hydrolysis catalyst
10 and the hydrogen sulphide absorbent were in the form of approximately spherical granules of diameter in the range 2.5 to 5 mm.

The process was found to be beneficial to the performance of a sulphur sensitive catalyst in a down-stream operation.

Claims

1. A process for the removal of carbonyl sulphide from a fluid stream comprising passing the fluid through a fixed bed of an intimate mixture of shaped units formed from particles of a carbonyl sulphide hydrolysis catalyst and shaped units formed from particles of an absorbent for hydrogen sulphide.
2. A process according to claim 1 wherein the shaped units have maxima and minima dimensions in the range 0.5 to 6 mm and an aspect ratio below 2.
3. A process according to claim 1 or claim 2 wherein the maximum dimension of the absorbent units is 0.5 to 2 times the maximum dimension of the hydrolysis catalyst units.
4. A process according to any one of claims 1 to 3 wherein the hydrolysis catalyst units form 5 to 50% by volume of the mixture of units.
5. A process according to any one of claims 1 to 4 wherein the hydrolysis catalyst units are formed from an activated alumina composition and contain 0 to 10% by weight of a binder.
6. A process according to claim 5 wherein the hydrolysis catalyst units have a BET surface area of above 50 m²/g.
7. A process according to any one of claims 1 to 6 wherein the hydrogen sulphide absorbent is formed from a composition containing copper and/or zinc oxides, hydroxides, carbonates or hydroxycarbonates.
8. A process according to claim 7 wherein the absorbent also contains alumina.
9. A process according to any one of claims 1 to 8 wherein the feedstock is passed through the bed at a temperature ranging from 20°C to 200°C.

INTERNATIONAL SEARCH REPORT

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B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	FR 2 574 310 A (ELF AQUITAINE) 13 June 1986 (1986-06-13) page 5, line 19 - line 34	1,5-9
Y	US 5 853 681 A (WOOD PETER ET AL) 29 December 1998 (1998-12-29) column 4, line 15 - line 44	1,5-9
A	EP 0 698 577 A (BOC GROUP INC) 28 February 1996 (1996-02-28) claims 1,2	1-9
A	EP 0 218 153 A (BASF AG) 15 April 1987 (1987-04-15) claim 1	1-9

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
FR 2574310	A	13-06-1986	FR 2574310 A1	13-06-1986
US 5853681	A	29-12-1998	AT 166596 T	15-06-1998
			AU 686759 B2	12-02-1998
			AU 1819795 A	03-10-1995
			CA 2183734 A1	21-09-1995
			DE 69502711 D1	02-07-1998
			DE 69502711 T2	24-09-1998
			DK 750524 T3	15-02-1999
			EP 0750524 A1	02-01-1997
			ES 2116732 T3	16-07-1998
			WO 9524962 A1	21-09-1995
			JP 9510141 T	14-10-1997
			NO 963875 A	16-09-1996
			ZA 9501890 A	18-09-1995
EP 0698577	A	28-02-1996	US 5674463 A	07-10-1997
			CN 1120517 A ,B	17-04-1996
			DE 69523695 D1	13-12-2001
			DE 69523695 T2	01-08-2002
			EP 0698577 A1	28-02-1996
			ZA 9506152 A	04-06-1996
EP 0218153	A	15-04-1987	DE 3534741 A1	09-04-1987
			EP 0218153 A2	15-04-1987